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**US 4394251**

**US 4309276**

**US 4309275**

**US 4370219**

(58) Field of search

**C5E**

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(54) **Process for the catalytic cracking of light distillates**

(57) Light distillates obtained in the petroleum industry or petrochemical industry are submitted to catalytic cracking in the presence of crystalline silica polymorph of the silicalite type, in the presence of water at a mola ratio of water:distillate of 0.5 to 5, at a temperature of 450°C to 600°C, and the isobutylene formed is recovered from the gaseous products obtained.

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## SPECIFICATION

**Process for the catalytic cracking of light distillates**

5 The present invention relates to a process for the cracking of light distillates obtained in the petroleum industry or petrochemical industry. It relates more especially to a process for the production of isobutylene by the catalytic cracking of light distillates such as straight-run gasolines or naphthas or fractions obtained in certain petrochemical operations and having a similar boiling range to these gasolines and naphthas.

10 At the present time, butylenes (this term including 1-butylene, cis- and trans-2-butylene and isobutylene) are obtained by extraction from cracked gases, especially those obtained in the production of ethylene by the pyrolysis of naphthas and the like. These gases consist of a mixture containing mainly ethylene and propylene, and their butylene content does not generally exceed about 8% by volume.

25 Subjecting naphthas to catalytic cracking instead of thermal pyrolysis favours the formation of products having a higher content of hydrocarbons containing 3 and 4 carbon atoms and of middle distillates and gasolines.

30 Thus, the catalytic cracking of naphtha with a moving bed catalyst gives a product which can contain up to 12% of butylenes. However, the isobutylene content of this mixture of butylenes does not generally exceed 25%.

35 It can therefore be seen that the cracking processes used hitherto, whether thermal or catalytic, give only small quantities of isobutylene.

Now, isobutylene is used for the manufacture of important industrial products such as tert.-butyl alcohol (solvent), tert.-butylphenol and methylene-bis-tert.-butylphenol (antioxidants and stabilizers) and low molecular weight polymers (for improving the viscosity index of lubricating oils). Furthermore, the measures taken against the use of tetraethyl lead in fuels have made it necessary for the petroleum industry to study other additives, especially oxygen-containing additives, for improving the octane number of fuels. Of these additives, asymmetric ethers, including methyl tert.-butyl ether (or MTBE) in particular, have proved very effective. MTBE is prepared from methanol and isobutylene.

55 Consequently, the present quantities of isobutylene available do not enable these derivatives to be produced in sufficient quantities to satisfy the potential market. It is therefore of value to be able to provide a method enabling isobutylene to be obtained simply and economically.

60 The present invention relates to a new process for the catalytic cracking of light distillates from the petroleum or petrochemical industry. It also relates to a process for crack-

ing these light distillates which favours the formation of isobutylene.

According to the present invention there is provided a process for the catalytic cracking of light distillates, which process comprises carrying out the cracking of the light distillates in the presence of crystalline silica polymorph of the silicalite type, in the presence of water at a molar ratio of water:distillate of 0.5 to 5, at a temperature of the order of 450° to 600°C, and recovering isobutylene from the gaseous products obtained.

The said light distillates can consist of fractions obtained in a refinery from the distillation of crude oils and having a boiling range of the order of 15° to 175°C. These light distillates consist of fractions generally known as gasoline, light naphtha and heavy naphtha. The process of the invention can also be applied to light distillates obtained from certain operations in the petrochemical industry, for example from the oligomerization of olefins. In a preferred embodiment of the invention, the distillates subjected to catalytic cracking are obtained as by-products in the processes for the production of isobutylene, either from propylene or by the isomerization of n-butenes. These processes are described in our Luxembourg Patents Nos. 85.284 and 85.285.

The catalyst is a crystalline, unmodified polymorphous silica of the silicalite type. It is therefore a virtually pure silica, which means that it does not contain any modifying elements or impurities or only contains them in trace amounts. The method of preparation and the structure of silicalite are described in U.S. Patent 4,061,724 in the name of Grose, which is mentioned herein by way of reference.

105 The distillate cracking reaction is carried out in the presence of silicalite and steam. It has in fact been found, unexpectedly, that the presence of steam permits a substantial increase in the production of isobutylene. Furthermore, the presence of steam makes it possible to increase the life of the catalyst by reducing the deposition of deactivating heavy products on the catalyst. This results in a better selectivity in respect of isobutylene, i.e. an increase in the quantity by weight of isobutylene formed, calculated relative to 100 parts by weight of converted distillate. These improvements are already obtained when the cracking of the light distillate takes place in the presence of a quantity of the order of 0.5 mol of water per mol of distillate. Comparative experiments have also shown that molar ratios of water:distillate of more than 5 bring scarcely any advantages. In the case where the process is applied in the preferred embodiment mentioned above, the molar ratio of water:distillate is kept at a value of from 0.5 to 3, and preferably from 0.75 to 2.

130 The temperature at which the catalytic

cracking is carried out can vary from 450° to 600°C. Temperatures below 450°C only give low yields and temperatures above 600°C cause degradation of the reaction products. As a general rule, a pyrolysis temperature of the order of 475° to 550°C will be used.

The hourly space velocity of the feedstock, expressed as the quantity by weight of feedstock per hour and per unit weight of catalyst (or WHSV), can vary within wide limits. It depends especially on the nature of the feedstock and the cracking temperature. A reduced space velocity, especially of less than 2, can result in degradation of the products. On the other hand, an excessively high space velocity does not enable a good pyrolysis ratio to be obtained. Thus, a space velocity of from 2 to 20 and most frequently of the order of 5 to 15 is maintained.

In a preferred embodiment of the process of the present invention, the light distillates subjected to catalytic cracking are obtained as by-products in the production of isobutylene, either from a feedstock containing propylene or from a feedstock containing n-butenes. These light distillates have a boiling range of the order of 35° to 195°C and represent a very valuable feedstock. In fact, treating them by the process of the invention forms a further quantity of isobutylene. Thus, by combining the processes, particularly high yields of isobutylene are obtained from propylene or n-butenes. The processes can be combined in this way using two reactors in series, the first being used to treat the feedstock containing propylene or n-butenes, with the formation of isobutylene, and the second being used to carry out the catalytic cracking of the distillates formed as by-products in the first reactor. Another embodiment consists in carrying out the two steps of these combined processes in a single reactor operating under adiabatic conditions and having an appropriate temperature profile.

The following Examples illustrate the present invention.

#### Example 1

A feedstock comprising 28.93% (by weight) of propane and 71.07% of propylene was treated in the presence of silicalite and steam, using a molar ratio of water:feedstock of 0.78, at a temperature of 303°C and an absolute pressure of 14 bar and with a WHSV of 79.8.

This gave isobutylene and a light distillate with selectivities of 11.3% and 64.6% respectively. This distillate has a boiling range of from 36° to 196°C.

The process of the present invention was then applied by treating this distillate in the presence of silicalite and steam, at a molar ratio of water:distillate of 1.26, at a temperature of 550°C and an absolute pressure of 2 bar and with a WHSV of 9.91.

This gave isobutylene with a selectivity of 18.1%.

#### Example 2

A feedstock comprising 5.84% (by weight) of propane and 94.16% of propylene was treated in the presence of silicalite and steam, using a molar ratio of water:feedstock of 0.92, at a temperature of 316°C and an absolute pressure of 4 bar and at a WHSV of 35.6.

This gave isobutylene and a light distillate with selectivities of 12.4% and 62.8% respectively. This distillate has a boiling range of from 36° to 196°C.

The process of the present invention was then applied by treating this distillate in the presence of silicalite and steam, at a molar ratio of water:distillate of 2.71, at a temperature of 500°C and an absolute pressure of 5.4 bar and with a WHSV of 8.57.

This gave isobutylene with a selectivity of 12.8%.

#### CLAIMS

1. A process for the catalytic cracking of light distillates obtained in the petroleum industry or petrochemical industry and having a boiling range similar to gasolines and naphthas, which process comprises performing the cracking of the said light distillates in the presence of a crystalline silica polymorph of the silicalite type, in the presence of water at a molar ratio of water:distillate of 0.5 to 5, at a temperature of 450° to 600°C, and recovering isobutylene from the gaseous products obtained.

2. A process according to Claim 1, wherein the light distillates which are subjected to catalytic cracking have a boiling range of 15° to 175°C.

3. A process according to Claim 2, wherein the light distillate which is subjected to catalytic cracking is obtained as a by-product in the production of isobutylene from propylene.

4. A process according to Claim 2, wherein the light distillate which is subjected to catalytic cracking is obtained as a by-product in the production of isobutylene by the isomerization of n-butenes.

5. A process according to any one of the preceding Claims, wherein the molar ratio of water:distillate is from 0.5 to 3.

6. A process according to Claim 5, wherein the molar ratio of water:distillate is from 0.75 to 2.

7. A process according to any one of the preceding Claims, wherein the catalytic cracking is carried out at a temperature of 475° to 550°C.

8. A process according to any one of the preceding Claims, wherein the catalytic cracking is carried out at an hourly space velocity, expressed as the quantity by weight of feeds-

tock per hour and per unit weight of catalyst,  
of from 2 to 20.

9. A process according to Claim 8,  
wherein the hourly space velocity is from 5 to  
5 15.

10. A process for the catalytic cracking of  
light distillates obtained in the petroleum in-  
dustry or petrochemical industry and having a  
boiling range similar to gasolines and na-  
10 phthas, substantially as hereinbefore de-  
scribed in Example 1 or 2.

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